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STRUCTURAL MODIFICATIONS OF PYRRHOTITE AT PYRITE-PYRRHOTITE DEPOSITS OF THE MALÉ KARPATY MTS.

(Fig. 1—15)

Abstract: The Malé Karpaty pyrite deposits are considered as exhalative-sedimentary, genetically linked with the submarine diabase volcanism of Lower Paleozoic age. The sulphide sulphur with negative δS^{34} values is of biogenic origin.

In periplutonically metamorphosed parts of the productive zones hexagonal and monoclinic pyrrhotites occur. Purely monoclinic pyrrhotites without accompanying hexagonal ones are quite rare. Ores exclusively formed by the hexagonal type have not been found.

Characteristic of the ore mineralization of the Malé Karpaty Mts. is the common occurrence of both structural types, with quantitative prevalence of the hexagonal type. According to the interplanar spacings values the content of Fe attains in it 47,3—47,4 at. %.

Both structural types also differ in the character of distribution of Ni, Co and obviously also of other microelements. This is the result of different genetical conditions and structures:

In hexagonal pyrrhotites, as a consequence of more stable P-T-conditions of formation, of ordered structures and a more uniform offer of Ni and Co, the limits of variations in Ni and Co (as well as of other minor elements) contents are relatively narrow.

Monoclinic pyrrhotites are on the contrary characterized by greater variability in Ni and Co contents: as a consequence of abundant lattice defects, lower thermality as well as of variable offer of Ni, Co and trace elements in general during their formation.

At the Malé Karpaty deposits the later origin of monoclinic pyrrhotite may be traced very well, starting from grain boundaries and fissures in the hexagonal type. We suppose that this transformation took place by the action of relatively low-tempered probably carbonate-bearing solutions on hexagonal pyrrhotites. A part of Fe was carried away and the newly formed monoclinic pyrrhotites are also characterized by different pattern of microelements distribution.

Резюме: В метаморфически измененных участках сульфидных месторождений Малых Карпат находятся гексагональная и моноклинная модификации пирротина; в составе руд преобладает гексагональная фаза, в которой содержание Fe достигает 47,3—47,4 ат. %. Моноклинный пирротин возникает позже, замещением и его появление поступает от края зерен и трещин в гексагональной модификации под влиянием низкотемпературных, вероятно карбонатных растворов. Действием этих растворов Fe из гексагонального пирротина выносится и изменяется характер разделения микроэлементов в отдельных модификациях. В следствие различных условий образования и типа структуры моноклинный пирротин отличается от гексагонального большей изменчивостью содержания Ni и Co.

Introduction

The minerals of pyrrhotite-troilite group are marked not only by complexity of structures but also by variability of chemical composition. The beginnings of detailed investigation of some aspects of this group reach back to the 30-ies. However, mainly

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in the last decade an uncommon upswing of theoretical investigation of the individual members of the group and the Fe-S system in general as well as of studies and interpretations of members occurring under natural conditions set in.

Pyrrhotite is often found in various genetical types of West Carpathian deposits, in ore indications as well as accessory mineral, mainly in metabasic rocks.

On representation of individual structural types of pyrrhotite in the West Carpathian system data of any kind have been lacking until lately. The first information in this regard has been supplied by the study of the authors of this article (J. Kantor — J. Ďurkovičová 1973, in press) dealing in detail with distribution of monoclinic and hexagonal pyrrhotites and their mutual relations at the Heľpa deposit. It has been established that the hexagonal pyrrhotite is an older product of metamorphism; the monoclinic originated by its replacement — by removal of Fe by lower-temperature solutions. Similar conditions have also been found in the limited sample material also from other pyrite and pyrite-polymetallic deposits (e. g. Zlaté Hory). Regarding to the differences in genetical conditions of both structural types of pyrrhotite the view of unequal possibilities of entrance of trace elements in their lattices and consequently also of the need of separate investigation of microelements distribution in hexagonal and monoclinic pyrrhotites has been expressed.

The present article is a continuation in our investigation of structural types and provides results on a more detailed study from the pyrite-pyrrhotite deposits of the Malé Karpaty area.

Geological setting and ore deposits

The works striving to clear up geological development and ore deposits in our westernmost Core Mountains — the Malé Karpaty Mts. — are dated back to the half of the last century (F. Andrian — C. M. Paul 1864). Continuing are sporadical investigations of H. Beck — H. Vetters (1904), R. Lachmann (1915), V. Zoubek — J. Koutek (1936) and others. They all provided results, correspondent to the time, in which the investigations were carried out, and to the applied methods of research.

The year 1950 brought a turn to systematic investigation of the Malé Karpaty crystalline and its metallogenesis. In it participated in the first place B. Cambel (B. Cambel 1950, 1954, 1956, 1960, B. Cambel — G. Kupčo 1952, 1965, B. Cambel — M. Böhmer 1955, B. Cambel — J. Valach 1956, B. Cambel — J. Jarkovský 1967, 1969, St. Polák 1956a, b, I. Čillík — P. Sobolič — R. Žákovský 1959, R. Žákovský 1962).

Owing to these authors the Malé Karpaty Mts. at present belong to the most thoroughly studied areas of the West Carpathian crystalline. In the light of their investigations the geological structure appears as follows:

The essential part of the crystalline is formed by granitoids:

1. The Modra Massif in the north, mainly represented by biotite granodiorites. Subordinately more leucocratic two-mica granodiorites are found there.

2. Bratislava Massif, more extensive, in the southern part of the mountains. It consists of muscovite-biotite-quartz granodiorites with local development of two-mica granites. In the massif are abundant pegmatite vein bodies.

The crystalline is mainly developed in the Pezinok-Pernek area in the depression separating both granitoid massives as well as along the western margin of the Bratislava Massif. In the granitoid intrusions blocks of the crystalline schists of various size are also found.

The crystalline schists are of purely sedimentary as well as volcanogenic origin. They originated from predominantly psammitic, more subordinately from pelitic sediments, alternatig as a consequence of flyschoid sedimentation. In places accumulation of organogenic material took place, from which graphitic schists have formed.

The eruptive components of crystalline schists formed due to intense manifestations of basic, submarine volcanism. From sediments with small admixture of pyroclastic material originated quartz-actinolite phyllites; from pyroclastics — actino-schists. The amphibolites correspond to former effusive members of diabase volcanism whilst the spotted amphibolites with feldspar phenocrysts are considered as its metamorphosed, hypabyssal members.

According to investigations of B. Cambel the Malé Karpaty crystalline was characterized by regional epimetamorphism prior to the intrusions of granitoids. Its grade increased (meso- to cata-) as a consequence of periplutonic contact metamorphism by Variscan granitoids, from which biotite mica-schists to gneisses resulted.

The effusive-sedimentary complexes are considered as Lower Paleozoic — Devonian in age. In favour of such an assignment points B. Cambels find of Devonian crinoids from carbonate sediments of the Harmonia (epimetamorphic) Group.

Pyrite deposits are found in the Pezinok-Pernek section of the crystalline in the so called productive complex consisting of actinolite and graphite schists. This is incorporated between the so called underlying and overlying amphibolites, which represent mightier effusions of diabase rocks.

According to the geological maps five zones of more or less mineralized actinolite and graphite schists are exposed, converging in strike toward the SE part of the Pezinok-Pernek crystalline.

The genesis of deposits was not sufficiently cleared up for a long time and the pyrite-pyrrhotite mineralization was ascribed a hydrothermal or liquation origin; the latter obviously because investigation was restricted to material of dumps from high-grade metamorphosed parts.

Only on the basis of rich material from extensive bore-holes and mine workings it was possible to arrive to the present-day view of exhalative-sedimentary origin of ore mineralization (St. Polák 1956, B. Cambel 1956).

The mentioned zones of productive actinolite-graphite schists are the bearers of all significant accumulations of pyrite ores.

The southernmost of them is interrupted by an offshoot of granitoid intrusion in the central part. In its southeastern segment are found pyrite and antimonite deposits (Ferdinand, Karol, Pod Kolárskym vrchom), in the northwestern segment is located the pyrite deposit of Turecký vrch ((Rudolf).

The more northerly lying productive zone (fig. 1) contains the mightiest ore bodies of the Malé Karpaty crystalline — the deposit Augustín, which in SE direction is linked with less important mineralized sections Nádej and Kristína. This area is pierced by several granitoid bodies and displays highest metamorphism of pyrite ores manifested in abundant representation of pyrrhotite. Toward NW the intensity of metamorphism decreases: west of the Mt. Čmele slightly altered pyrite-graphite-quartz ores occur (St. Polák 1956).

A lower grade of metamorphism display also ores of the Pernek deposit, where with pyrite also Sb-ores were exploited.

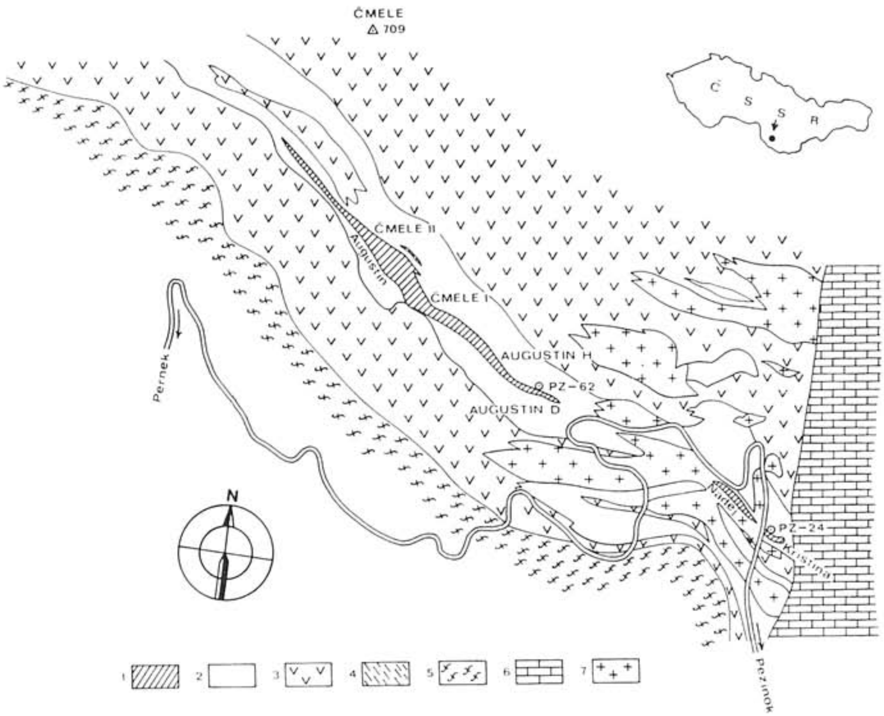


Fig. 1. Geological sketch map of the environs of the deposit Augustín in Pezinok. Modified from B. Cambel, St. Polák and R. Žákovský. Explanations: 1 — pyrite-pyrrhotite deposit, 2 — actinolite schists, 3 — amphibolites, 4 — graphite schists, 5 — biotite phyllites, mica-schists and gneisses, 6 — Mesozoic of the Malé Karpaty envelope unit, 7 — granitoid rocks.

The last productive zone — of Kuchyňa — contains pyrite and Sb-mineralization of little importance.

The common occurrence of both types of ores (FeS_2, Sb) in the same productive zones also at the same deposits is a feature remarkable of the Malé Karpaty metallogenesis. So far it has been explained by superimposition of younger, postgranitic hydrothermal ore mineralization on older exhalative-sedimentary type of pyrite mineralization (B. Cambel 1956, R. Žákovský 1962, St. Polák 1956a).

One of the authors of this article (J. K.) has proved that in pyrites of these ores sulphur of biogenic origin dominates and is not lacking even in some Sb-minerals (J. Kantor — B. Cambel 1972). This fact as well as the tendency to consider the Silurian also in the area of neighbouring Austria as significant bearer of syngenetic Sb-accumulations (A. Maucher 1965, A. Maucher — R. Höll 1968) require a more profound study of this problem. For the time being at the Dionýz Štúr Institute of Geology investigation of sulphur isotopes distribution is being continued particularly regarding to light biogenic sulphur and to possible processes of its assimilation by granitoid magma and remobilization.

Mineral composition of ores

The paragenetic association of sulphide minerals at the pyrite deposits is simple: in little metamorphosed types of ores pyrite is almost the only sulphide. Insignificant amounts of chalcopyrite and sphalerite are usually associated with it. The contents of Cu and Zn vary in hundredths of per cent and only exceptionally reach tenths.

In intensely metamorphosed parts of productive zones pyrrhotite becomes more important, as it is particularly the case in the area of the deposits Augustín, Nádej and Kristína. In places pyrite mineralization may be almost lacking there.

Other members of paragenetic associations are nonmetallic minerals, which are commonly met in the country rocks of sedimentary, volcanic-sedimentary or only volcanic origin. They occur in ores in very variable amounts: in rich, compact ores they are little represented, in poor impregnation ores forming the essential portion of mineralized material. They are mainly quartz, graphite, actinolite, amphiboles, biotite, muscovite, chlorite, carbonates, rutile, ilmenite, etc.

According to mineral composition belong to industrial types quartz-sulphide, quartz-graphite-sulphide and amphibole-sulphide ores. They all can be mutually linked with gradual transition.

Accessory sulphides are practically found in all rock types of the Malé Karpaty crystalline.

Although pyrrhotite is a significant mineral of the Malé Karpaty pyrite deposits, except for a brief note of the authors of this article (J. Kantor — J. Ďurkovičová 1973), any other published data regarding its structural type are lacking. To clear up this fact we examined material of various genetic origin and were more in detail focused on the largest accumulations of this mineral from the area of the Augustín deposit.

For identification of these individual structural types the method of magnetite suspensions, etching by means of HI and CrO_3, X-ray diffractometer data and partly also electron microprobe analyses were applied.

The diffractograms were obtained by aid of diffractometer Mikrometa II with goniometer GON-03 of the firma Chirana and with FeKα radiation. The shift of goniometer was $1/4°2\theta$ in a min. with a rate of record 600 mm/per hour. At the diffractograms in the $55-57°/2\theta$ interval hexagonal pyrrhotites are marked by one peak corresponding to d (102); monoclinic ones by two peaks with equal intensity for d (202) and d $(20\bar{2})$.

Corresponding to the mixtures of both structural types of pyrrhotite are diffractograms with the first peak (lower values of 2θ) exceeding the second one. The ratio of reflection intensities is proportional to percentage representation of hexagonal modification in the mixture (fig. 2).

From the diffractograms the values for d (102) + d (202), d $(20\bar{2})$ as well as the average value d (102) + (202) + $(20\bar{2})$ measured below the level of resolved $20\bar{2}$ reflections were calculated. As internal standard was used Brasilian quartz with a value $54.17°2\vartheta$/FeKα for the (202) reflection, which served for calibration.

The results are summarized in table 1, where beside the d-values are given in the last column also approximated percentage contents of hexagonal modification in mixtures of both types of pyrrhotite.

In one sample no. 6 with the value d (202) = 2.060 Å is present exclusively monoclinic pyrrhotite. In other samples d (102) + (202) varies from 2.062 to 2.067 Å and the analysed material represents a mixture, in which the hexagonal modification mostly predominates over the monoclinic one.

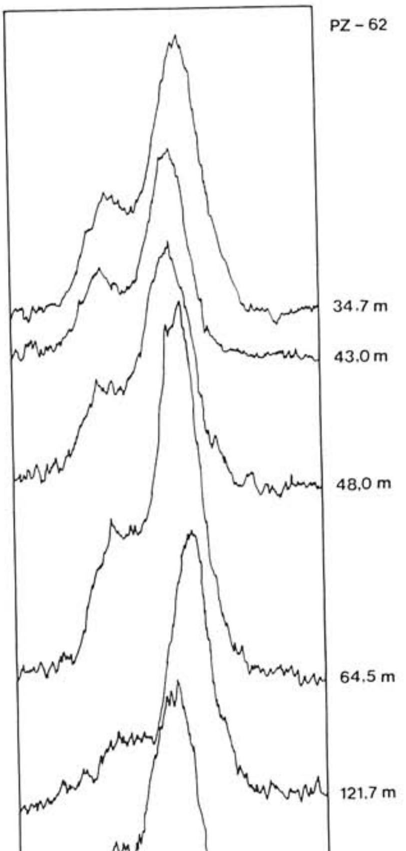


Fig. 2. X-ray diffractogram of reflections (102), (202), (202) of pyrrhotites from borehole PZ-62.

In table 1 are also given the values for pyrrhotites from borehole PZ-62 penetrating across a mighty ore lenticle of the deposit Augustín (fig. 3). Corresponding diffractograms according to depth are presented in fig. 2. According to records of the members of the Geological Exploration pyrrhotite at this deposit is mainly found in marginal parts, more in the upper part of ore bodies. Represented are both modifications. A similar situation we meet also at the deposit Kristína (fig. 4), where the samples were taken not far away from the granitoid body.

When the method of R. G. Arnold — L. E. Reichen (1962) is applied, for iron-richest hexagonal pyrrhotites we examined from the Malé Karpaty region Fe contents up to 47.3—47.4 atomic % result. The same upper boundary was also found in hexagonal pyrrhotites from Heľpa (J. Kantor — J. Ďurkovičová l. c.).

Microscopically identified hexagonal pyrrhotite (fig. 6) from a sample of the boring PZ-62 has been analysed for the Fe and S contents by the microprobe technique too (J. Krištín). Results: 61,44 wt. % of iron and 39,46 wt. % of sulphur. The corresponding crystallochemical formula $Fe_{8,94}S_{10,00}$ is in good accordance with the X-ray data.

Mutual relations between hexagonal and monoclinic pyrrhotites were studied under the microscope by means of magnetite suspension and etching.

Ores containing only the monoclinic type are rare in the Malé Karpaty Mts. — sometimes they are found in disseminated, poor ore mineralizations and among accessory sulphides.

So far we have not been able to find ores with the hexagonal modification as only representative of pyrrhotite though it distinctly predominates in the Malé Karpaty.

Pyrrhotites of this area are mixtures of both structural types. Their quantitative ratios are variable also at very small distances.

The most frequently present mutual relation is shown in the microphotograph fig. 5. In greater accumulations of hexagonal pyrrhotite narrow vein-like bodies of monoclinic

Table 1

No	d (102) + (202)	d (20$\bar{2}$)	d (102) + (202) + (20$\bar{2}$)	% hex. po
1	2,065	2,050	2,058	80
2	2,065	2,052	2,061	60
3	2,067	2,054	2,062	70
4	2,063	2,051	2,058	50
5	2,062	2,049	2,057	40
5a	2,062	2,050	2,058	40
5b	2,064	2,051	2,059	55
6	2,060	2,050	2,055	0
7	2,065	2,051	2,060	60
8	2,063	2,049	2,057	60
9	2,062	2,049	2,057	50
10	2,064	2,052	2,058	60
11	2,065	2,052	2,060	75
12	2,062	2,050	2,057	40
13	2,064	2,050	2,060	60
14	2,062	2,051	2,058	30

Explanations: 1 — Bratislava, Železná studienka, quarry, 2 — Lamač, crematorium, quarry, 3 — Cajla, Čmele II-adit, 4 — Cajla, Augustín horná-adit, 5 — Cajla, Augustín horná-adit, 6 — Cajla, Augustín horná-adit, 7 — Cajla, Augustín deposit, boring PZ-62, 34,7 m, 8 — Do, 43,0 m, 9 — Do, 48,0 m, 10 — Do, 64,5 m, 11 — Do, 121,7 m, 12 — Do, 131,0 m; 13 — Cajla; Rýhova-adit, 14 — Cajla, Kristína deposit, boring PZ-24, 25,6 m.

modification develop along fissures and grain boundaries. With proceeding alternation they may by extended.

In fig. 6 hexagonal pyrrhotite in the form of irregular corroded grains with lobate delimination amidst the monoclinic type is shown.

The marginal parts of grains of hexagonal pyrrhotite are usually replaced by monoclinic one — fig. 7.

In translationally twinned grains some parts may be also replaced by monoclinic pyrrhotite, whilst in adjacent grains an intact, hexagonal modification is preserved (fig. 8, right and left of the centre).

Monoclinic pyrrhotite sometimes forms also along the contact of hexagonal pyrrhotite with other minerals, e. g. chalcopyrite (fig. 9, 10).

The mentioned relations are generally common in the ores of the Malé Karpaty Mts. They testify to an earlier origin of hexagonal pyrrhotite and its subsequent replacement by monoclinic modification.

Already St. Polák (1956) called attention to the fact that in epimetamorphosed crystalline sulphides of the deposits as well as accessory ones are represented by pyrite; in parts with intense periplutonic metamorphism caused by granitoid intrusion — by pyrrhotite in turn. Although this dependence is obvious, in close vicinity of many veins and apophyses of granodiorite intersecting the pyrite deposits, no alteration of pyrite into pyrrhotite has been observed. So he concludes that pyrrhotinization was supported by the thermal effect of granitoid magma, combined with the action of easily volatile constituents.

Although the processes leading to transformation of pyrite into pyrrhotite may be not cleared up in details, our investigations show that perhaps without exception in

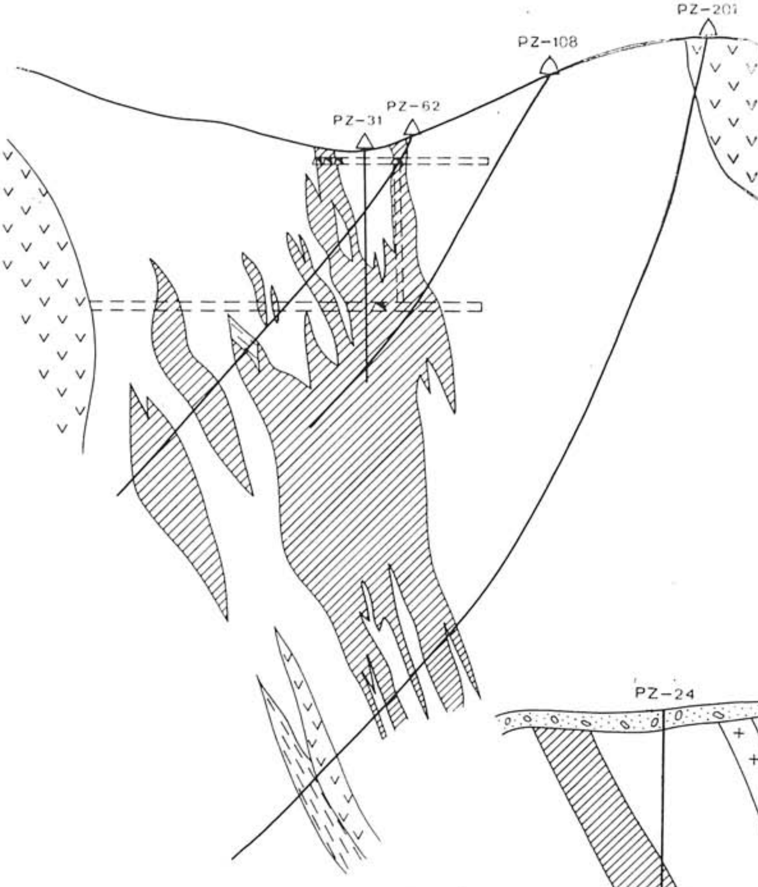


Fig. 3. Vertical section through the deposit Augustín in Pezinok, according to St. Polák. Explanations like in fig. 1.

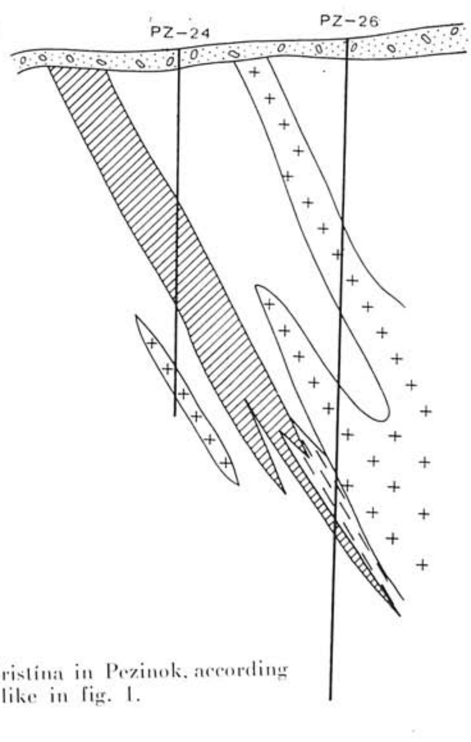


Fig. 4. Vertical section through the deposit Kristína in Pezinok, according to St. Polák. Explanations like in fig. 1.

Fig. 5. Hexagonal pyrrhotite in initial stage of replacement by monoclinic modification (dark-grey) along fissures and grain boundaries. Covered with magnetite suspension. Pezinok, borehole PZ-62, polished section, magnif. 150 ×

Fig. 6. Relics of hexagonal pyrrhotite (light-grey) in monoclinic pyrrhotite (light-darker-grey spotted, covered by magnetite powder) Amphiboles, quartz — blackish-grey. Pezinok, borehole PZ-62, polished section, magn. 150 ×.

Fig. 7. Hexagonal pyrrhotite replaced from the margins by monoclinic (magnetic domains covered with magnetite — dark-grey). Lamač, quarry near the crematorium, polished section, magnif. 150 ×.

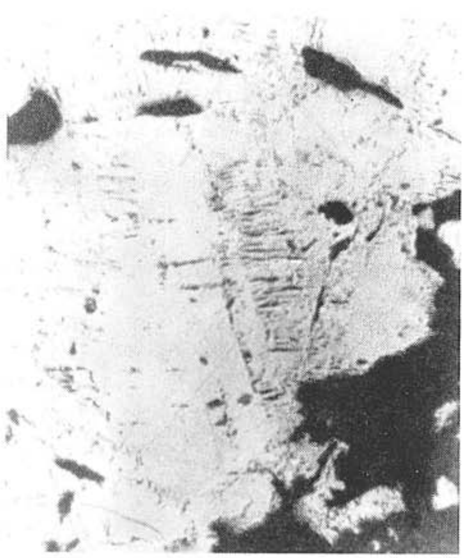


Fig. 8. Hexagonal pyrrhotite with patches of monoclinic modification. The latter originated in the translationally twinned part (right from the centre — covered with magnetite). Pezinok, Augustín adit. Polished section, magnif. 110 ×.

Fig. 9. Space between porphyroblasts of amphibole (black) filled in with pyrrhotite and chalcopyrite. In hexagonal pyrrhotite along fissures, margins and the contact with chalcopyrite is developed a narrow rim of monoclinic pyrrhotite (dark-grey — covered with magnetite). Pezinok, Rýhova adit, polished section, magnif. 150 ×.

Fig. 10. Like fig. 9 — detail. Contact of hexagonal pyrrhotite with chalcopyrite bordered by monoclinic modification. Polished section, magnif. 450 ×.

the first stage hexagonal pyrrhotite originated with higher Fe content up to 47.3—47.4 atomic %.

As far as pentlandite is present in pyrrhotite, always its hexagonal modification is concerned. Pentlandite has not been known from the Malé Karpaty region so far. We have found it among accessory sulphides from amphibolites. Most often it occurs in the shape of typical bush-like forms (fig. 11) or in flame-like shaps not rarely near microdislocations and fissures (fig. 12), scarcerly also in the shape of elongated, rodlike forms (fig. 13).

Monoclinic pyrrhotite is characterized by high contents of sulphur and lower ones of iron. In the Malé Karpaty region there exist differences both in the age as well as in the Fe and S contents between hexagonal and monoclinic pyrrhotites. Both may be explained by later removal of Fe from hexagonal pyrrhotite by the effect of relatively low-temperature waters.

Such an origin of monoclinic pyrrhotite was postulated first by A. D. Genkin et al. (1965) for some deposits of the Soviet Union and by the authors of this article for the pyrrhotite-pyrite deposit of Heľpa (J. Kantor — J. Ďurkovičová 1973).

Such a possibility has been demonstrated experimentally by the action of sodium bicarbonate solutions on hexagonal pyrrhotite in the temperature interval 175—200 °C (O. Oelsner — R. Starke 1964).

In the course of our investigations we had a very restricted but welcomed possibility

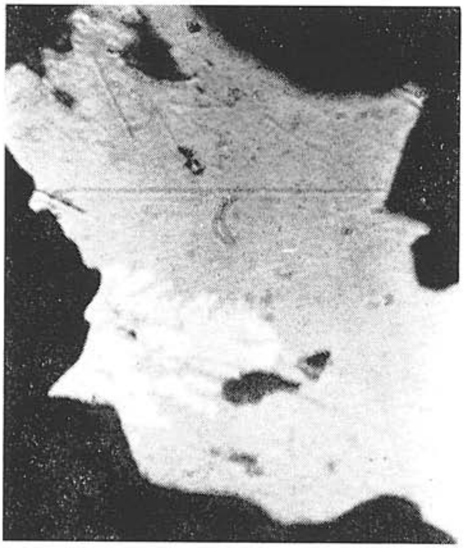


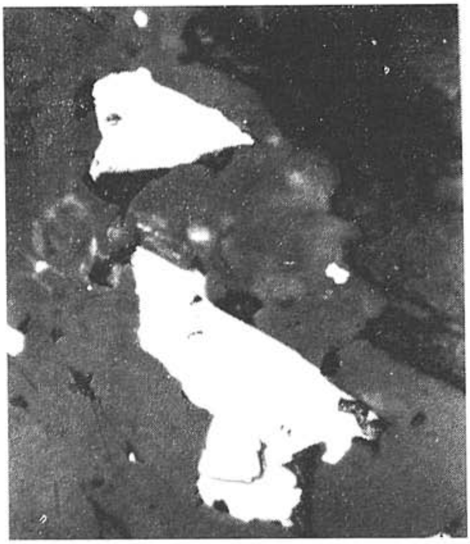
Fig. 11. Hexagonal pyrrhotite with common type bush-shaped pentlandite. Bratislava, quarry in the Vydrica Valley, polished section, magnif. 1300 ×.

Fig. 12. Hexagonal pyrrhotite with pentlandite (white) and silicates (black). Locality like fig. 11, Microprobe, 21 kV, magnif. 300 ×.

of analyses on the microprobe, for which we also express our thanks to J. Krištín. The results are summarized in table 2.

The sample no. 1/10 is an accessory hexagonal pyrrhotite from amphibolites. It contains pentlantide (fig. 12, 14). Remarkable is the relatively high content of Co, in spite of that impregnations in a small block of amphibolites enclave in the Bratislava granitoid massif are concerned. In pyrrhotite with analogous geological position from Rača near Bratislava B. Cambel — J. Jarkovský (1969) found similar concentrations of Co and they seem not to be rare here. For the majority of pyrrhotites however — also from intensely metamorphosed parts of the crystalline — they report essentially lower Co contents. Therefore there seem to exist enough exceptions to the tendency of decrease in Co contents in pyrrhotites with increasing intensity of metamorphism quoted by them.

For other samples quoted in table 2 the chemical composition is always given for the hexagonal modification (sub a) and monoclinic (sub b), found in direct contact with the foregoing one. Comparison of these two analyses shows that hexagonal pyrrhotites are marked by a more stable chemical composition and their Ni- and Co-contents (and obviously of other elements too) vary within narrow limits. In monoclinic pyrrhotites the contrary is found and in the samples analysed by us also a tendency to a decrease of Ni in contrast to the hexagonal modification may be observed. In sample 6/14 the content of Ni varied at the level of background only. The last sample — a poor impregnation ore in actinolite schist; the foregoing two rich pyrite-pyrrhotite ores.



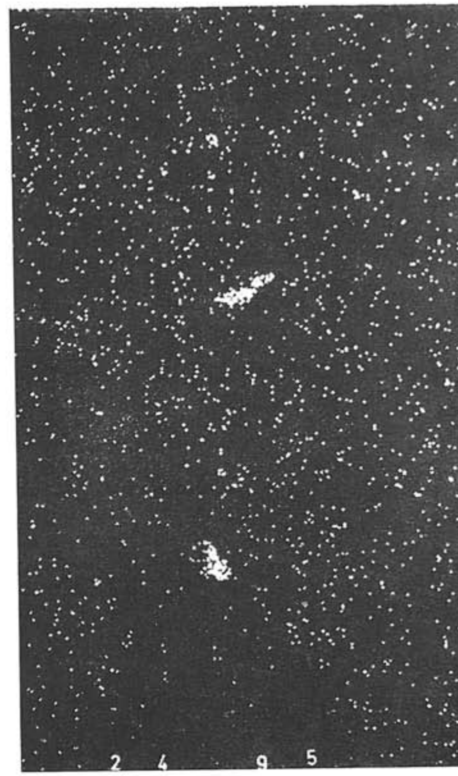


Fig. 13. Pyrrhotite-pyrite impregnations in amphibolite. In pyrrhotite elongated pentlandite. Locality like in fig. 11. Polished section, magn. 600 ×.

Fig. 14. Like fig. 12. Distribution of nickel, NiK_{α}. Microprobe, 21 kV.

The differences in chemical composition are in good accordance with different genetic compositions: a) in hexagonal pyrrhotites with higher thermality, ordered lattice, more uniform and stable offer of Ni and Co during the formation of pyrrhotite, b) in monoclinic pyrrhotites with lower thermality, more abundant defects in the structure, more variable offer and mobility of elements during leaching and transition of hexagonal into monoclinic modification.

Quite equal tendencies in the Ni contents as those found by us in Malé Karpaty ore mineralizations are mentioned from the deposit Strathcona mine, Sudbury in Canada by D. S. Vaughan et al. (1971). The absolute contents of Ni are, of course, higher regarding to the different genetic type of deposit.

Both structural types of pyrrhotite of the Talnakh Cu-Ni deposit in the USSR, which are found there in 3 generations, were also examined for the contents of Ni and Co by microprobe (N. N. Šiškin et al. 1972). Also here hexagonal pyrrhotites are characterized by less variability, mainly in Ni contents, than the monoclinic ones. In contrast to the Malé Karpaty Mts. and Strathcona mine, however, the absolute amounts of Ni in hexagonal pyrrhotites are lower.

In figure 15 are compared the ranges of Ni and Co concentrations found by us in the Malé Karpaty hexagonal and monoclinic pyrrhotites with the results mentioned by B. Cambel — J. Jarkovský (l. c.) on the basis of spectral analyses of mixtures of both modifications. Regarding to the fact that purely monoclinic or hexagonal modifications and the application of the microprobe are concerned in one case,

Table 2

	No	Ni (%)		Co (%)		Struct. type
		range	∅	range	∅	
Malé Karpaty Mts.[1]	1/10	0,27—0,50	0,41	0,13—0,19	0,16	hex.
	4/8a	0,28—0,41	0,39	tr.	tr.	hex.
	13/22a	0,31—0,38	0,35	tr.	tr.	hex.
	62/131a	0,41—0,48	0,44	tr.		hex.
	62/8a	0,25—0,33	0,29	tr.		hex.
	4/8b	0,24—0,44	0,35	tr.		mon.
	13/22b	0,03—0,36	0,28	0,00—0,06	0,03	mon.
	62/131b	0,19—0,49	0,33	tr.		mon.
	62/8b	0,01—0,64	0,23	tr.		mon.
	6/14	tr.	tr.	tr.	tr.	mon.
Talnakh deposit[2] USSR	I. gen.	0,14—0,32	0,24	0,03—0,06	0,05	hex.
	II. gen.	0,15—0,33	0,22	0,03—0,06	0,05	hex.
	III. gen.	0,15—0,20	0,18		0,04	hex.
	I. gen.	0,19—0,92	0,41	0,03—0,08	0,06	mon.
	II. gen.	0,18—0,90	0,39	0,05—0,07	0,06	mon.
	III. gen.	0,13—0,23	0,18	0,05—0,07	0,06	mon.
Strathcona mine[3], Sudbury, Canada		0,68—1,01	0,85			hex.
		0,36—1,04	0,50			mon.

[1] This paper, [2] N. N. Šiškin et al. 1972, values for various generations, [3] D. S. Vaughan et al. 1971.

mixtures of both modifications and spectral analyses in the latter case, the accordance of results, mainly as to variation ranges in chemical composition is relatively good.

Our investigations have shown the existence of differences in the character of Ni and Co distribution between hexagonal and monoclinic pyrrhotites from the Malé Karpaty Mts. The established variation ranges are based on a relatively small number of analyses. Further systematic investigation of a larger number of suitably chosen samples can therefore bring more precision in our data, mainly as to the limits of contents.

In the foregoing work (J. Kantor—J. Ďurkovičová l. c.) we pointed to the existence of monoclinic and hexagonal pyrrhotites at the metamorphosed pyrrhotite-pyrite deposit of Hefpa in the Nízke Tatry Mts. In the character of distribution of both modifications in Hefpa certain differences between various parts of the deposit were observed. The western deposit is formed by hexagonal as well as monoclinic pyrrhotite: the eastern one almost exclusively by monoclinic modification with sporadical relics of the hexagonal. Monoclinic pyrrhotite is also a typical representative of poor impregnation ores and accessory sulphides from rocks.

In mightier sulphidic bodies hexagonal pyrrhotite shows a tendency to richer repre-

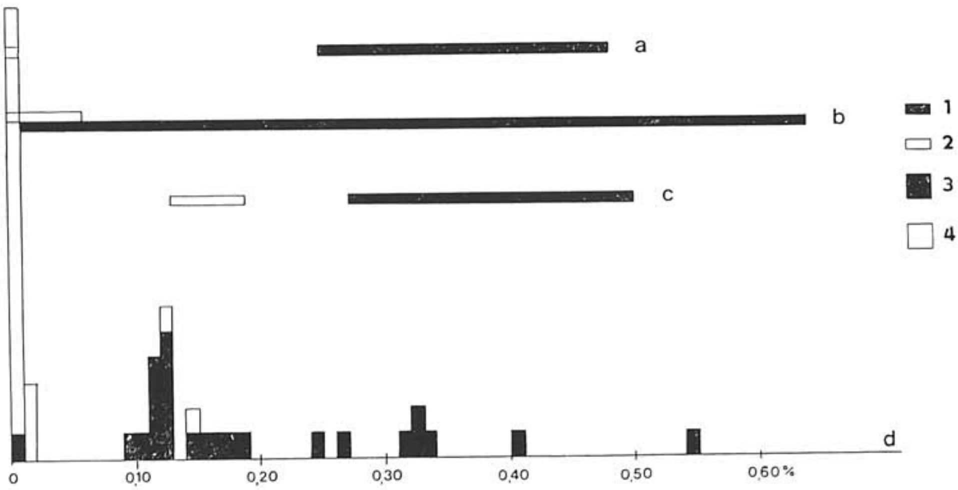


Fig. 15. Distribution of Ni and Co in pyrrhotites. Variation according to microprobe analysis (J. Kantor — J. Ďurkovičová): 1 — Ni, 2 — Co, a — hexagonal pyrrhotite from deposit, b — monoclinic pyrrhotite from deposit, c — hexagonal pyrrhotites, accessory, from amphibolite, 3 — Ni, 4 — Co, 3,4 — histograms of mixtures of monoclinic and hexagonal modifications according to spectral analyses (B. Cambel — J. Jarkovský 1969).

sentation in central parts: monoclinic pyrrhotite rather along the margins of ore bodies. On the whole the monoclinic variety is predominating at the Hefpa deposit.

In the Malé Karpaty Mts. we have also found hexagonal as well as monoclinic type of pyrrhotite. Purely monoclinic pyrrhotite is quite rare here. Usually a mixture of both is found. In contrast to Hefpa, in the Malé Karpaty ores hexagonal pyrrhotite is more distinctly represented. Apparent is here also its replacement by later — monoclinic type.

Conclusion

The Malé Karpaty pyrite deposits are considered as exhalative-sedimentary, genetically linked with Lower Paleozoic submarine volcanism of diabase character. Sulphur of biogenic origin (negative δS^{34} values) is for the sulphides characteristic.

In parts with more intense periplutonic metamorphism of productive zones pyrrhotite is abundantly found. It is usually represented by both structural types: hexagonal and monoclinic.

Purely monoclinic pyrrhotites without accompanying hexagonal are quite rare. They were observed only in poor, impregnation types of ore mineralization.

Exclusively hexagonal types have not been found so far as well, beside which monoclinic types did not occur, at least in subordinate amounts.

Characteristic of the Malé Karpaty ore mineralization is the common occurrence of both structural types, with the hexagonal predominating quantitatively. Mutual ratio is very variable and varying even in microscopic dimensions.

On the basis of X-ray data the content of Fe in hexagonal pyrrhotites reached 47.3—47.4 atomic %.

Both structural types also differ in the character of distribution of Ni, Co and obviously also of other microelements as result of different genetic conditions and structures:

In hexagonal pyrrhotites, as a consequence of more stable P-T conditions during formation, of ordered structures and more equable „offer" of Ni and Co, their chemical composition is more stable, and the variation ranges of Ni and Co contents are relatively narrow.

Monoclinic pyrrhotites, on the contrary, are marked by greater variability in Ni and Co contents. This follows from abundant lattice defects, lower thermality and variable offer of Ni, Co and trace elements in general in the course of their formation.

At the Malé Karpaty deposits the later formation of monoclinic pyrrhotite is apparent, starting from the margins of grains and fissures in the hexagonal type of pyrrhotite. We suppose that this alteration took place by the effect of relatively low-temperature, probably carbonate-bearing solutions on hexagonal pyrrhotites. A part of Fe was carried away and in the newly formed monoclinic pyrrhotites which are characterized by lower iron contents also a different pattern of microelements distribution resulted.

Translated by J. PEVNÝ.

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Review by B. CAMBEL.